Continuous and discontinuous grain-boundary wetting in Zn$_x$Al$_{1-x}$

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Temperature dependences of the contact angle $\theta(T)$ between (i) specially grown tilt grain boundaries (GBs) in Al and the Zn-rich melt; (ii) tilt GBs in Zn and the Al-rich melt; and (iii) tilt GBs in Zn and the Al-based solid solution (Al)$_x$ were measured using scanning electron microscopy and light microscopy. $\theta$ decreases with increasing $T$ in all cases and reaches zero (complete wetting) at a certain temperature $T_w$ in cases (i) and (ii). The wetting transformation for Al GBs is discontinuous (first order): $\theta(T)$ dependence is convex, $d\theta/dT$ has a break at $T_w$, and $\theta^2-(T-T_w)/T_w<\frac{1}{2}$. The wetting transformation for Zn GBs is continuous: $\theta(T)$ dependence is concave, $d\theta/dT$ is continuous at $T_w$, and $\theta^2-(T-T_w)/T_w<\frac{1}{2}$. For the Zn GBs in contact with a second solid phase (Al)$_x$, $\theta(T)$ dependence is concave and $\theta^2-(T-T_w)/T_w<\frac{1}{2}$ for the extrapolated $T_w$. The observed change from the discontinuous wetting transition for GBs in a metal with a higher melting point (Al) to the continuous one for GBs in a metal with a lower melting point (Zn) is explained using the approach proposed in [Pandit et al., Phys. Rev. B 26, 5112 (1982)]. The validity of this approach and critical exponent of 3/2 may indicate that GB wetting in the Zn-rich alloys is governed by the long-range forces.

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I. INTRODUCTION

For the liquid droplet on a solid substrate, two situations are possible. If a liquid spreads on the surface, then one can speak about full (or complete) wetting. The contact angle between liquid and solid in this case is zero. If a liquid droplet does not spread and forms a finite contact angle, then it is a partial (or incomplete) wetting. Cahn’s idea was the “driving force” for the experimental finding of GB wetting phase transformations, initially made in Zn-Sn, Zn-Sn-Pb, and Ag-Pb polycrystals. At a later stage, the original experimental data were reconsidered from this point of view and numerous indications on the GB wetting phase transformations were found, particularly for Zn-Sn, Al-Cd, Al-In, Al-Pb, W-Ni, W-Cu, W-Fe, Mo-Ni, Mo-Cu, and Mo-Fe (Ref. 11) polycrystals. The exact measurements of the temperature dependence for the GB contact angle with the melt were made using the individual GBs in the specially grown bicrystals in the Cu-In, Al-Sn, and Zn-Sn (Ref. 14) systems. Cahn’s generic phase diagram also predicted that the tie line of the wetting transition in the two-phase region continues in the one-phase (solid solution) area as a prewetting line. Between the prewetting line and the solubility limit for a solid solution, the surface contains a thin (liquidlike) layer of a phase, which is not stable in the bulk. The experimental evidence of such prewetting (or premelting) layers was also found in GBs in the Fe-Si-Zn, Cu-Bi, and Al-Zn (Ref. 19) systems and semiconductors such as Y$_2$O$_3$-doped AlN, La-doped SrTiO$_3$, Bi$_2$O$_3$-doped ZnO, and Ca-doped Si$_3$N$_4$. Wetting and prewetting (premelting) phase transformations drastically change the GB properties such as diffusivity, mobility, strength, segregation, and conductivity. GB wetting phenomena play an important role for the liquid-phase sintering of metals and ceramics, semisolid metal processing, thixotropic casting, and the exploitation of heat-exchanger tubes filled with liquid metal in nuclear plants, etc.

All these mentioned surface and GB wetting phase transformations are of first order (discontinuous), which means that discontinuity of the first derivative of surface (or GB) energy occurs at $T_w$. However, the wetting transitions of a higher order are also possible. In other words, the first derivative of surface (or GB) energy remains continuous at $T_w$ but their higher derivatives have a break. The continuous wetting phase transitions were theoretically predicted in Refs. 32–34 and for a long time remained a topic for the very intensive theoretic investigations (see also Ref. 7 for the review). Indeed, the continuous wetting phase transition was first observed experimentally only in 1996. Up to now, all continuous wetting phase transitions were observed for the alcanes in contact with methanol, water, or brine liquid/liquid systems, which are technologically important for oil recovery. The continuous thickness divergence of the al-
cane layer on water or brine substrate was observed as long-range critical wetting due to the long-range van der Waals forces. It is usually preceded by the first-order thin-thick transition in the adsorbed alcane layer leading to the appearance of the mesoscopic film on the water or brine surface. These experiments supported further theoretical developments. However, the data obtained on a rather restricted number of a very similar binary liquid systems remained up to now a single array of experimental observations of continuous wetting transformations. At the end of an excellent review by Bonn and Ross, it was stated that “similar results in a different kind of system, in particular a solid substrate system, would be very interesting to see.”

This work is devoted to the experimental observation of the first-order and continuous GB wetting in the Al-Zn system using the individual GBs in the specially grown Al and Zn bicrystals. From the bulk Al-Zn phase diagram (Fig. 1), it is obvious that the Al-Zn system belongs to the “classical” Cahn’s systems with a critical point for a binary solution. It was previously observed in experiments with polycrystals that in the (Al)+L two-phase region, the GB transformation for the Al GBs wetting by Zn-containing melt occurs. (Al) is the Al-based Al+Zn solid solution. Below \( T_{s\text{GB}} \approx 440 ^\circ\text{C} \), completely wetted GBs in the Al-Zn polycrystals do not exist. \( T_{s\text{GB}} \) is the wetting temperature for a GB with maximal energy \( \sigma_{\text{GB max}} \). Above \( T_{s\text{GB}100\%} = 565 ^\circ\text{C} \), all high-angle GBs in (Al) are wetted by the melt (Fig. 2). \( T_{s\text{GB}100\%} \) is the wetting temperature for a GB with minimal energy \( \sigma_{\text{GB min}} \). Between \( T_{s\text{GB}} \) and \( T_{s\text{GB}100\%} \), the wetting tie lines for GBs with intermediate \( \sigma_{\text{GB max}} > \sigma_{\text{GB}} > \sigma_{\text{GB min}} \) are positioned in the (Al)+L area. GB triple junctions (TJs) become completely wetted at the temperature \( T_{s\text{TI100\%}} = 555 ^\circ\text{C} \) below \( T_{s\text{GB}100\%} \). According to Cahn’s generic phase diagram, the GB wetting tie lines continue as prewetting (or premelting) lines in the one-phase (Al) area. Just one prewetting line for \( T_{s\text{GB}} \) is shown for simplicity in Fig. 1. The experimental evidence for the existence of a GB liquid-like phase between GB prewetting line and bulk solidus line was obtained by transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) (open triangles in Fig. 1). It was also observed that the second solid phase (Al) can completely wet the GBs in (Zn) polycrystals (Zn) is the Zn-based Zn+Al solid solution. (Al) and (Al) are the isomorphous Al-based solid solutions with low- and high-Zn content, respectively, below the critical point \( T_e = 351.5 ^\circ\text{C} \) (Fig. 1). Below \( T_{w\text{GB}100\%} = 290 ^\circ\text{C} \), no (Zn) GBs completely wetted by the (Al) solid phase exist in the (Zn)+(Al) polycrystals. Above \( T_{w\text{GB}100\%} \), the (Zn) GBs completely wetted by the (Al) solid phase appear in the (Zn)+(Al) polycrystals. The amount of completely wetted (Zn) increases with increasing temperature and reaches about 30% at eutectic temperature \( T_e = 381 ^\circ\text{C} \). Thus, the majority of (Zn) GBs remain incompletely wetted by the (Al) solid phase at \( T_e \) and the tie line \( T_{w\text{GB}100\%} \) is not present in the (Al)+(Zn) two-phase region of the Al-Zn phase diagram (Fig. 1). However, experimental evidence was obtained which indicated that the (Al) phase with low-Zn concentration does not completely wet the (Zn) GBs in the (Al)+(Zn) two-phase region below the temperature \( T_{\text{min}} = 277 ^\circ\text{C} \) of monotectoid transformation. The same is also true for the opposite side of the (Al)+(Zn) two-phase region. In other words, the (Zn) solid phase cannot completely wet the GBs in the (Al) phase.

II. EXPERIMENT

Flat Al and Zn bicrystals having a thickness of 2 mm, a width of 10 mm, and a length of 50–100 mm with individual tilt GBs were grown from the Al and Zn of 99.999 at. % purity using the modified Bridgman technique. Two \( \langle 110 \rangle \) tilt GBs with misorientation angles \( \phi = 15 ^\circ \) and \( 35 ^\circ \) in Al and three \( \langle 1120 \rangle \) tilt GBs with misorientation angles \( \phi = 11.5 ^\circ \), \( 46 ^\circ \), and \( 84 ^\circ \) in Zn were grown. Since tilt GBs with different \( \phi \) possess different energy \( \sigma_{\text{GB}} \), we also expected different \( T_{s\text{GB}} \) values for them. The bicrystals were cut into pieces of 10-mm length. The layer of the (Al)+(Zn) alloy of nearly eutectic composition was applied on two opposite surfaces of each 2 × 10 × 10 mm Al and Zn bicrystal. Individual 2 × 10 × 10 mm Al and Zn bicrystals coated by a
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III. EXPERIMENTAL RESULTS

The contact angle $\theta$ decreases with increasing temperature in all three experimental series [Figs. 4(a)–4(c)]. In the case of Al GBs, the contact angle starts from about $\theta=80^\circ$, decreases with increasing temperature, and reaches $\theta=0^\circ$ at $T_{w15^\circ}=525$ °C for $\phi=15^\circ$ and at $T_{w35^\circ}=530$ °C for $\phi=35^\circ$ [Fig. 4(a)]. Above $T_{w15^\circ}$ and $T_{w35^\circ}$, the contact angle remains zero. Both $T_{w15^\circ}$ and $T_{w35^\circ}$ lie between $T_{w=GB100^\circ}$ and $T_{w=GB100^\circ}$ (Fig. 1). The $\theta(T)$ dependence for both Al GBs is convex. The first temperature derivative of each $\theta(T)$ dependence (and, respectively, of the GB energy) has a break at $T_{w15^\circ}$ and $T_{w35^\circ}$. The convex shape and the break of the temperature derivative for $\theta(T)$ were predicted for the first-order (discontinuous) wetting transitions. In the case of the liquid-phase wetting of Zn GBs, the contact angle starts from about $\theta=80^\circ$, decreases with increasing temperature, and reaches $\theta=0^\circ$ at $T_{w46^\circ}=T_{w11.5^\circ}=415$ °C for $\phi=46^\circ$ and $\phi=11.5^\circ$ and at $T_{w84^\circ}=418$ °C for $\phi=84^\circ$ [Fig. 4(b)]. Above $T_{w46^\circ}$, $T_{w11.5^\circ}$, and $T_{w84^\circ}$, the contact angle remains zero. The $\theta(T)$ dependence for all three Zn GBs is concave. The first temperature derivative of each $\theta(T)$ dependence (and, respectively, of the GB energy) remains continuous at $T_{w46^\circ}$, $T_{w11.5^\circ}$, and $T_{w84^\circ}$. The concave shape and the continuity of the temperature derivative for $\theta(T)$ were predicted for the second-order (continuous) wetting transitions. [5]
In the case of the solid-phase wetting of Zn GBs, the contact angle starts from about $\theta=80^\circ$, decreases with increasing temperature, and reaches $\theta=37^\circ$ for the GB with $\phi=46^\circ$ and $\theta=28^\circ$ for the GB with $\phi=84^\circ$ at $T=370^\circC$. In other words, both studied GBs belong to the majority of GBs, which remain partially wetted by a second solid phase (Al)$^{\text{II}}$ below $T_c$. However, the $\theta(T)$ dependence for both Zn GBs is concave. As mentioned above, the concave shape is an indication of the second-order (continuous) wetting transitions.$^5$

### IV. DISCUSSION

The convex shape and the break of the temperature derivative for $\theta(T)$ are usual for the GB wetting phase transformations.$^8$–$^{14}$ However, the concave shape and the continuous temperature derivative for $\theta(T)$ are observed for the GB wetting. Theory also predicts different critical exponents, namely, 1/2 for the discontinuous and 3/2 for the continuous wetting transitions.$^5$ In Fig. 5 the measured $\theta(T)$ dependences (Fig. 4) are presented in the scaling coordinates $\log \theta - \log (T - T_c)/T_c$. Data for Al GBs fit well to the slope 1/2 [Fig. 5(a)]. A line with the slope 3/2 is also shown for comparison. In other words, the scaling condition for the discontinuous transition is fulfilled for the wetting of Al GBs by the Zn-rich melt. The scaling exponent of 1/2 for GB wetting transition was also observed for similar tilt Al GBs wetted by the Sn-rich melt.$^{13}$ Temperature dependences $\theta(T)$ for two different tilt GBs were convex and the break of the temperature derivative for $\theta(T)$ was also present.$^{13}$

Data for Zn GBs fit well to the slope 3/2 [Figs. 5(b) and 5(c)]. It concerns both GB wetting by a liquid phase (filled symbols) and by a second solid phase (open symbols). The extrapolated values $T_{\text{w46}}=415^\circC$ and $T_{\text{w84}}=410^\circC$ were used for the GB wetting in Zn by the (Al)$^\text{I}$ solid phase [Figs. 5(b) and 5(c)]. Lines with the slope 1/2 are also shown for comparison. In other words, the scaling condition for the continuous transition is fulfilled for the wetting of Zn GBs by the Al-rich melt and the (Al)$^\text{II}$ solid phase.

The experiments with Zn-5 wt % Al polycrystalline alloys showed that the first Zn/Zn GBs become completely wetted by the (Al)$^\text{I}$ solid phase at $T_{\text{w46}}=290^\circC$ (see also Fig. 1).$^{36}$ However, only about 30% of all Zn/Zn GBs become wetted at the eutectic temperature $T_e=381^\circC$. These GBs possess the highest energy among all GBs in Zn polycrystal. The Zn/Zn GBs with low energy (such as twin GBs) remained incompletely wetted at $T_e$. In the Al-rich alloys, all high-angle GBs become wetted above $T_{\text{w46}}=565^\circC$ (Fig. 1).$^{53}$ The minimum temperature of GB wetting phase transition for Al/Al GBs is $T_{\text{w46}}=440^\circC$ (Fig. 1).$^{10}$ The temperatures of GB wetting for tilt GBs grown in this work, $T_{\text{w35}}=530^\circC$ and $T_{\text{w15}}=525^\circC$, are very close to the maximum temperature $T_{\text{w46}}=565^\circC$ and are far away from the minimum one $T_{\text{w46}}=290^\circC$ (Fig. 1). On the other hand, it is known that the energy difference between GBs with the misorientation angles of 15° and 35° is maximal possible for the (110) tilt GBs.$^8$ It means that all tilt GBs possess rather low energies, comparable with general GBs in a polycrystal. Therefore, it is not surprising that all three [1120] tilt Zn GBs grown in this work belong to the 70% of GBs, which remain partially wetted at $T_e$. It is especially true since the 84° [1120] tilt GB is very close to the twin GB having minimum possible energy among all GBs in Zn. Therefore, the $T_{\text{w46}}$ value for such GBs was estimated using the extrapolation to the temperatures above $T_c$ [Figs. 4(c), 5(b), and 5(a)].

If the concave shape and the continuous temperature derivative for $\theta(T)$ [Figs. 4(b) and 4(c)] undoubtedly witness that the GB wetting transition in Zn-rich samples is continuous, then the scaling exponent of 3/2 [Figs. 5(b) and 5(c)] devotes more detailed discussion. Namely, the 3/2 exponent is predicted for critical wetting in systems whose wetting behavior is governed by long-range forces (more specifically nonretarded dispersion force) (see Sec. IVB of Ref. 5). How-
ever, wetting in metallic systems is usually thought to be controlled by short-range forces rather than by dispersion force and wetting theory does not predict a universal scaling exponent 3/2 for such systems (see Sec. IIIB-D of Ref. 5). Therefore, the observed 3/2 exponent could be either a coincidence or indeed an indication that long-range force controls the wetting behavior of Zn GB by Al melt. Surely, the second possibility would be more interesting. It can be experimentally checked, namely, since the dispersion force is also weak in metals, one can expect that Zn GBs will be quite thick (a few tens of atomic layers) just below the wetting point—similar to the mesoscale alkane films on water systems.38 The presence of “thick” GBs or GB prewetting films was already witnessed by both direct or indirect experiments in the metallic systems such as the Al-rich Al-Zn alloys,54,55,58 Cu-Bi,18,62 or Fe-Si-Zn alloys.15–17 The direct observation of the thick GBs in the Zn-rich Zn-Al alloys just below the wetting point would convincingly prove the importance of long-range force to GB wetting in metals. Such experiments using the synchrotron radiation will be performed by us soon. They have to be conducted in situ by the very exact temperature control.

Thus, we observed that in the Al-Zn system, the change from the discontinuous GB wetting in the Al-rich side to the continuous GB wetting in the Zn-rich side proceeds. In Ref. 63 the multilayer adsorption on attractive substrates was analyzed. Various combinations of substrate-liquid interaction energy and interaction between atoms in the liquid phase have been compared. It has been theoretically predicted that in the case of strong substrate-liquid interaction and weak liquid-liquid interaction, the wetting should be of the first order. However, if substrate-liquid interaction becomes weaker, then the wetting transition can become continuous.60 The interatomic force in a metal correlates well with a melting temperature. Similar to the ideas in Ref. 63, Al (Tem = 660.45 °C) can be considered as a stronger substrate and Zn (Tm = 419.58 °C) would represent a weaker one. The transition from Al GBs to Zn GBs leads to the change from discontinuous to continuous wetting. Again, similar to the case of critical exponent 3/2, Ref. 63 only considered the long-range interaction between substrate and adsorbate. On the first glance, it does not suit well metallic systems. Therefore, the future experimental search for possible thick GBs just below the wetting point in Zn-rich Zn-Al alloys will give the crucial proof for the presence of long-range interaction in metallic GBs.

Previously only the wetting of GBs in metals with high Tm by a melt based on a low-Tm metal has been studied (i.e., in a “large ear” of a eutectic phase diagram).8–14 Therefore, the convex θ(T) and discontinuities of dθ/dT at Tw are always observed (first-order transitions). Already an attempt to study the wetting of GBs in a low-Tm metal by a liquid phase containing atoms of a high-Tm metal enabled us to find the continuous GB wetting. Most probably, the continuous GB wetting transitions are hidden in the “small ears” of other eutectic phase diagrams.

V. CONCLUSIONS

By measuring the temperature dependences of the contact angle θ(T) between (i) specially grown tilt grain boundaries in Al and the Zn-rich melt; (ii) tilt GBs in Zn and the Al-rich melt; and (iii) tilt GBs in Zn and the Al-based solid solution (Al)9, the discontinuous and continuous GB wetting transitions were observed. The wetting transformation for Al GBs is discontinuous (first order): θ(T) dependence is convex, dθ/dT has a break at Tw, and θ~(T−Tw)/Tw. The wetting transformation for Zn GBs is continuous: θ(T) dependence is concave, dθ/dT is continuous at Tw, and θ~(T−Tw)/Tw. For the Zn GBs in contact with a second solid phase (Al)9, θ(T) dependence is concave and θ~(T−Tw)/Tw for the extrapolated Tw. The critical exponent of 3/2 may indicate that GB wetting in the Zn-rich alloys is governed by the long-range forces.

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